7. TRIM.FaTE MERCURY CASE STUDY

As discussed in Chapter 6, systematic model evaluation is an important step in determining if a model performs as expected. Model evaluation activities have been undertaken for the TRIM.FaTE module starting with the early model prototypes and have included case studies with organic chemicals. Consistent with SAB recommendations, OAQPS has continued its model evaluation activities for TRIM.FaTE Prototype V. As described in Chapter 6, OAQPS is performing a variety of evaluation activities, including a case study for mercury at a chlor-alkali plant in the U.S. This case study, currently in progress, will begin with data quality, mechanistic, and structural evaluations, which will improve understanding of the most important model processes and inputs and of the effects of varying the model's spatial and temporal resolution. After gaining an understanding of and confidence in the model's structure and performance, the case study will proceed to compare TRIM.FaTE outputs with environmental and biotic measurement data for the selected site as well as with outputs from other models. The case study site and conditions also serve as the basis for extensive testing, troubleshooting, and sensitivity analysis of TRIM.FaTE. This chapter provides summary information on the mercury case study, including the study objectives, information on selection of the study chemical and test site, and an overview of the evaluation activities. In the future, EPA may perform additional case studies and apply TRIM.FaTE to other chemicals (*e.g.*, dioxins) and other locations.

7.1 OBJECTIVES

The specific objectives of the TRIM.FaTE mercury case study are three-fold:

1. Demonstrate that TRIM.FaTE can be used effectively for metals and other inorganic chemicals;

2. Demonstrate that TRIM.FaTE can account for reversible transformation of chemicals and can track the environmental fate of transformation products; and

3. Test TRIM.FaTE and compare the results with measured data, as well as against modeled results from IEM2M (EPA's Indirect Exposure Methodology, as modified for mercury and applied in the *Mercury Study Report to Congress* (U.S. EPA 1997a)).

MERCURY

Mercury is one of the 188 HAPs listed under section 112(b) of the CAA, is one of 33 HAPs being addressed by the Integrated Urban Air Toxics Strategy under section 112(k) (U.S. EPA 1999e), is a pollutant of concern under the section 112(m) Great Waters program (U.S. EPA 1999b), and is one of the seven specific pollutants listed for source identification under section 112(c)(6). In addition, the findings of the *Mercury Study Report to Congress* (U.S. EPA 1997a) indicate that mercury air emissions may be deposited to water bodies, resulting in mercury uptake by fish. According to that report, ingestion of mercury-containing fish is a critical environmental pathway of concern for mercury-related health effects in humans, particularly developmental effects in children.

7.2 CASE STUDY CHEMICAL SELECTION

As part of the evaluation process for TRIM, EPA must test TRIM.FaTE with both organic and inorganic pollutants because of their distinctly different multimedia fate and transport properties. The EPA selected PAHs for an organic chemical test case, and the methodology and results of that testing were reported in the *1998 TRIM Status Report* (U.S. EPA 1998e). The Agency selected mercury as an inorganic chemical for testing TRIM.FaTE because of its fate and transport properties (*e.g.*, transformation to multiple chemical species), the concern for multipathway exposure (particularly through ingestion of fish), and the potential health effects associated with exposure.

7.3 CASE STUDY SITE SELECTION

After selecting mercury for this case study, the Agency evaluated different stationary sources of mercury that are significant on a national basis. The four types of stationary sources with the highest total national air emissions of mercury, based on the findings of the *Mercury Study Report to Congress* (U.S. EPA 1997a), are – in order of highest to lowest mercury emissions – electric utility plants, municipal waste combustors, medical waste incinerators, and chlor-alkali plants. Electric utility plants, which are addressed in section 112(n) of the CAA, are still undergoing evaluation by EPA for possible regulation of mercury air emissions. For municipal waste combustors and medical waste incinerators, national air emission standards have been promulgated under section 129 of the CAA, and these standards are expected to result in large reductions of mercury air emissions.

Chlor-alkali plants were selected for further assessment in the TRIM.FaTE case study because they are a large source of mercury air emissions and are not yet regulated for HAP emissions. In addition, these plants are more likely than other major mercury emission sources to pose localized health concerns as a result of their lower stack heights and relatively high estimated level of fugitive emissions.

The Agency selected a single chlor-alkali plant for the mercury case study after evaluating data availability for several sites. At the time of the site selection, 14 chlor-alkali plants were in operation in the United States. Mercury air emission estimates were available for all 14 plants; however, data on mercury levels in environmental media and biota were available for only two of the plants. Fish tissue, water quality, and air quality data had been collected for one of the two plants, but ultra-clean techniques were not used for collecting and analyzing the water samples. For the second plant, air quality, soil, fish tissue, sediment, and additional biotic data had been collected and analyzed. In addition, accumulation of mercury in environmental media and biota near the second plant was possible because the plant has been in operation since 1967. Because the data set for the second plant was more complete, of higher quality, and readily available for use, that chlor-alkali plant was selected for the mercury case study. A simplified map of the site area showing delineation of the parcels used for the case study is provided in Figure 7-1 (for a general discussion of the process of defining parcels, volume elements, and compartments for a TRIM.FaTE application, see Chapter 5 of TRIM.FaTE TSD Volume I).[1]

7.4 CASE STUDY EVALUATION ACTIVITIES

As part of the TRIM.FaTE mercury case study, several different types of analyses are being performed that correspond with the types of evaluations (i.e., mechanistic and data quality, structural, performance) described in Chapter 6. These analyses are described below. The model input values being developed for the TRIM.FaTE mercury study are documented in Appendix C. Some of these values will likely be revised over the course of the case study as better information is acquired.

7.4.1 MECHANISTIC AND DATA QUALITY, AND STRUCTURAL EVALUATIONS

Evaluating the quality of the input data for a given model application is an iterative process. A literature search is completed to determine the value and identify any available information on the predicted uncertainty or variability associated with that value. The current values resulting from our search are listed in Appendix C. Then, a sensitivity analysis will be performed for all of the parameters to evaluate how the uncertainty in an input value influences the model output. If a model input is very uncertain and this uncertainty significantly influences the model output, more research may be completed to refine that input value. Additionally, the stage 2 Monte Carlo analysis (described in Chapter 3 of this report and Chapter 6 of TRIM.FaTE TSD Volume I) will be performed on these critical input parameters.

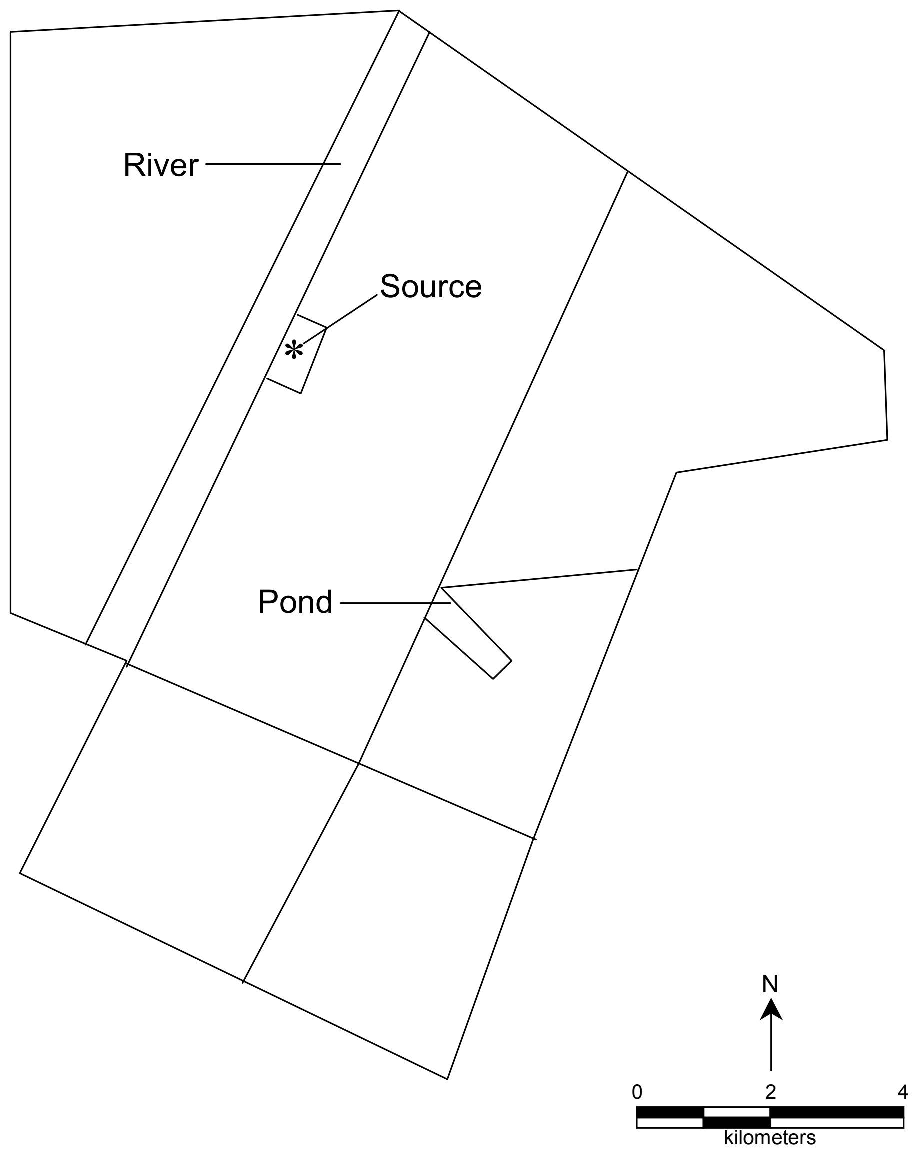
Evaluating the model's internal mechanisms (*i.e.*, mechanistic evaluation) involves assessing selected chemical fate and transport algorithms used in the model. In addition to assessing selected components of the model, intermediate processes, such as flows between compartments, will be assessed to ensure that the model accurately represents the current understanding of physical and chemical processes. It also must be confirmed that the algorithms work effectively together within the model. Because of the number of compartment types and links included in TRIM.FaTE, this will be a complex process.

One mechanistic evaluation being performed is a comparison of the TRIM.FaTE air component with a commonly used EPA air dispersion model, ISCST3 (U.S. EPA 1995c). Specifically, the concentration and deposition results from ISCST3 are being compared to the concentrations and total deposition fluxes estimated for the air compartments in TRIM.FaTE to provide insight into how the methodology for modeling transport and fate in TRIM.FaTE compares to the conventional Gaussian plume methodology used in ISCST3.

Another type of evaluation being performed in the TRIM.FaTE mercury case study is an assessment of the influence of the structural representation of the system being modeled. Some of the key assumptions in any TRIM.FaTE application, including this case study, involve

[1] While the case study site is a real facility and site-specific data are being used to the extent available, the name and location of the site are being kept confidential.

Figure 7-1
Simplified Parcel Layout for TRIM.FaTE Mercury Case Study[2]



[2] This diagram shows the initial set of surface water (*i.e.*, river, pond) and soil (*i.e.*, all other) parcels for the TRIM.FaTE mercury case study; the air parcels are slightly different. The Agency also plans to use more complex parcel layouts as the case study progresses.

determination of the simulation time step, the background and boundary concentrations, the spatial representation of the modeled system, and the compartment types selected for modeling. Examples of structural evaluation include the following:

- **Understanding the effect of temporal variability,** by assessing the impact of the temporal resolution of the meteorological and source emissions data on model outputs;

- **Understanding the effect of spatial configuration,** by comparing results obtained using a variety of spatial layouts; and

- **Determining the effect of external boundaries on internal compartments,** by assessing, for example, whether wind direction changes result in elevated concentrations in the air advected back into the system.

After the mechanistic and data quality, and structural evaluations are performed for the case study site, and greater understanding of and confidence in the model has been gained, the performance evaluation will begin.

7.4.2 PERFORMANCE EVALUATION

Model performance evaluation, as described in Chapter 6, can include comparisons of model outputs to outputs from other models and to available measurement data for a specific site. Both types of performance evaluations will be performed as part of the TRIM.FaTE mercury case study.

7.4.2.1 Comparison with Other Models

The objective of this part of the case study is to model environmental media and biota concentrations of mercury using ISCST3 and IEM2M for comparison to the fate and transport results from the TRIM.FaTE simulations. These models were selected as comparison benchmarks because they (or in case of IEM2M, the core model from which it was derived, IEM; see Section 2.1 of TRIM.FaTE TSD Volume I for more discussion of IEM) have been extensively reviewed and widely used by EPA to estimate air and multimedia fate and transport of air toxics for regulatory applications. Furthermore, IEM2M was applied previously by OAQPS in the *Mercury Study Report to Congress* (U.S. EPA 1997a). When possible, the inputs used for ISCST3/IEM2M will be identical to the TRIM.FaTE inputs in order to provide results that are most appropriate for comparison. In some cases, such as the spatial representation of the modeled system, this will not be possible because of fundamental differences in modeling approaches, and assumptions will be necessary to maximize the similarities between the models as applied.

Annual average air concentrations and deposition rates predicted by ISCST3 will be used as the chemical source inputs to the IEM2M fate and transport algorithms. Environmental media and biota concentrations predicted by IEM2M will be used for comparison to the corresponding TRIM.FaTE outputs. They also will be compared to a second set of TRIM.FaTE outputs generated using ISCST3 results as inputs instead of the built-in TRIM.FaTE air component. The fate and transport of three forms of mercury (*i.e.*, elemental, divalent, and methylmercury) will be tracked and compared. Because mercury speciation affects its fate and transport properties and because the speciation of the chlor-alkali source emissions is not known with certainty, two sets of simulations will be performed: (1) assuming that source emissions are composed of 100 percent elemental mercury (in gaseous form), and (2) assuming that source emissions are composed of 70 percent elemental mercury (in gaseous form) and 30 percent divalent mercury (in particulate form).

7.4.2.2 Comparison with Measurement Data

The objective of this part of the case study is to model environmental media and biota concentrations of mercury for the test site and compare the modeled outputs to the available monitoring data. Comparisons of multimedia model results to monitoring data are challenging because it is difficult to match modeling conditions to site conditions. However, these comparisons are useful analyses in the early stages of model evaluation and may lead to diagnostic assessments.

The parcels being modeled for the test site were constructed, in part, based on the available monitoring data so that data comparisons would be most relevant and meaningful. The results (*i.e.*, concentrations in environmental media and biota) from the TRIM.FaTE simulations will be compared to available measurement data for the chlor-alkali plant vicinity. Appendix D provides details on the abiotic and biotic monitoring data sets that are available for use in the TRIM.FaTE mercury case study. For each data set, Appendix D includes the following information: environmental medium, number of data points (including the number of duplicates and measurements below the detection limit), measurement endpoint(s) and units, sampling date(s), sample location(s), purpose of monitoring, range of values, mean and standard deviation of values, and other information (if relevant).

Some of the monitoring data sets are from on-site sampling that was conducted as part of site investigations in 1995 and 1997. In many cases, the on-site data sets also include at least one measurement from an off-site reference location. Most of the sample collection and analysis for the site investigations was performed by a contractor or by the facility. Several of the on-site sediment and surface water data sets that were available are not summarized in Appendix D because the data appear to represent mercury concentrations in waste streams, rather than mercury in the environment as a result of air emissions. There are also data sets from off-site locations, including additional data collected during the site investigations and data collected by independent researchers during monitoring efforts not related to the facility. Most of the available measurement data, however, are for total mercury, rather than being speciated into the various forms, which will limit direct comparisons to the speciated mercury results from TRIM.FaTE.

The abiotic environmental media data sets include both on-site and off-site monitoring data sets. The on-site monitoring data sets include five data sets for surface and subsurface soil measurements from various locations. The off-site monitoring data sets include ambient air mercury concentration measurements from three monitors within 7,000 feet of the facility;

surface water measurements from the adjacent river both downstream and upstream of the facility; and sediment measurements from four nearby ponds and lakes.

The biotic data sets also include on-site and off-site monitoring data sets. Deer mouse and earthworm tissue measurements from a variety of locations comprise the on-site data. Off-site data sets include various mercury concentration measurements in loons, including local level (*e.g.*, juvenile blood concentrations, adult male blood concentrations, egg concentrations from nearby ponds) and state level (*e.g.*, state average and individual site-specific juvenile, male adult, and female adult blood concentrations; state average egg concentrations) data. The off-site data sets also include measurements of mercury concentrations in skinless fillets of white perch from nearby ponds; mercury concentrations in short-tailed shrew tissues; mercury concentrations in eel tissues from the adjacent river; and a single measurement of the mercury concentration in a river minnow from the adjacent river. For full details on each of these on-site and off-site data sets, refer to Appendix D.